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Full configuration interaction potential energy curves for breaking bonds to hydrogen: An assessment of single-reference correlation methods

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Several approximate correlation methods have been assessed for bond breaking reactions in BH, HF, and CH_4 by comparison to the full configuration interaction limit. Second-order Møller–Plesset perturbation theory, coupled-cluster singles and doubles (CCSD), coupled-cluster with perturbative triples [CCSD(T)], and the hybrid density-functional method Becke three parameter Lee–Yang–Parr have been considered. Both restricted and unrestricted references have been used along with the basis sets aug-cc-pVQZ, 6-31G**, and 6-31G* for BH, HF, and CH_4 respectively. Among the methods considered, unrestricted CCSD and CCSD(T) provide potential energy curves which are the most parallel to the benchmark full CI curves, but the nonparallelity errors are fairly large (up to 6 and 4 kcal mol^{-1}, respectively). Optimized-orbital coupled-cluster methods provide superior results but nevertheless exhibit approximately the same maximum errors. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1531658]

I. INTRODUCTION

It is well known that restricted Hartree–Fock (RHF) is qualitatively incorrect for bond breaking, because near the dissociation limit there are two or more degenerate electronic configurations which cannot be described simultaneously by a single restricted Slater determinant. One may also note that, by constraining both electrons in the breaking bond to occupy the same spatial orbital, the RHF wave function contains unphysical ionic terms at long distances. Although unrestricted Hartree–Fock (UHF) can provide a potential-energy curve that breaks a bond qualitatively correctly, the results may be quantitatively poor, and the wave function is no longer an eigenfunction of $\hat{S}^2$. One might expect the inclusion of electron correlation to improve results for bond breaking, since additional electron configurations are included in the wave function, but this is not always the case. Indeed, RHF-based second-order Møller–Plesset perturbation theory gives energies which diverge to negative infinity at the dissociation limit. While multireference methods like CASPT2[1] can handle any type of bond breaking problem in principle, in practice the computations can become intractable if large active spaces are required. Hence, an economical and reliable description of bond breaking remains a challenge for electronic structure theory.

Within the Born–Oppenheimer approximation, the full configuration interaction (FCI) model represents the exact solution of the electronic Schrödinger equation for the chosen one electron basis set. Because its computational cost increases factorially with the number of electrons or orbitals, full CI computations are only feasible for small chemical systems with moderately sized basis sets. Nevertheless, full CI benchmarks are invaluable for assessing the intrinsic errors in various approximate models of electron correlation. They are particularly valuable for generating potential energy curves, since they do not suffer from the multiconfigurational nature of the wave function near the dissociation limit. Several previous studies have provided full configuration interaction (CI) energies at a few (often three) geometries along a potential energy curve.[2–6]

Advances in algorithms and computer hardware have recently made it possible to obtain more complete full CI potential energy curves[7–12] for some simple systems. For example, Olsen and co-workers have presented very useful polarized double-zeta full CI potential energy curves for bond breaking in several electronic states of the N_2 molecule[10,11] and full CI energies for five geometries along the symmetric dissociation (breaking both bonds) of H_2O. The benchmark full CI results were compared to perturbation theory and coupled-cluster models to indicate how these approximate methods perform for very challenging cases. Such benchmarks are essential for the calibration of new theoretical models meant to describe bond breaking processes.[13–18]

The present scarcity of such benchmark potential energy curves makes it unclear how well many of the standard correlation methods perform for different types of bond breaking. In the present study, we present full CI potential energy curves for three molecules (BH, HF, CH_4) in which a bond to hydrogen is broken. This should represent a common, chemically important process which one might expect to be the easiest bond breaking process for standard quantum-chemical methods to describe accurately. We compare various approximations to the full CI results, including second-order Møller–Plesset perturbation theory (MP2),[19] coupled-cluster singles and doubles (CCSD),[20,21] coupled-cluster singles and doubles with perturbative triples [CCSD(T)],[22] and the B3LYP gradient-corrected hybrid density-functional theory model.[23,24] Both restricted and unrestricted orbitals are considered.

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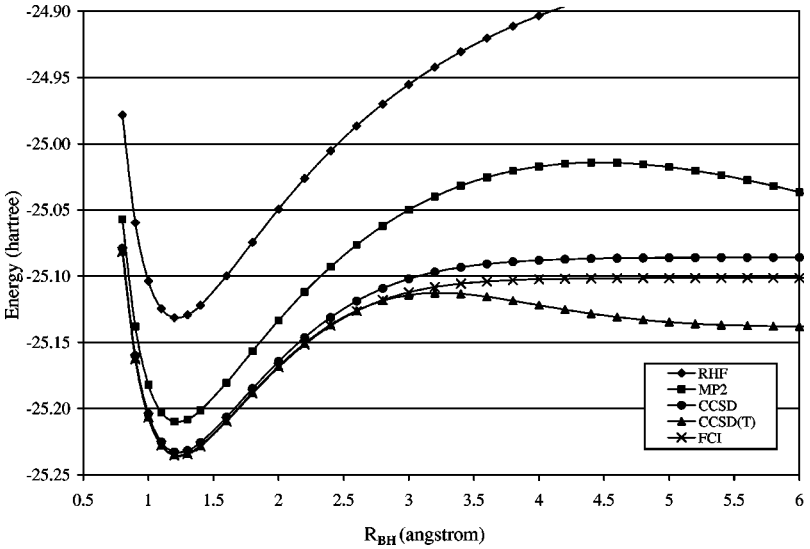

FIG. 1. Potential energy curves for BH in an aug-cc-pVQZ basis using full configuration interaction and various approximate correlation methods with an RHF reference.

Previous high-quality benchmarks for the molecules considered in this study include double zeta plus polarization (DZP) FCI results for three geometries of HF,[2] a DZP FCI potential energy curve for BH[9], and 6-311++G(df,p) multireference CI results[25] for the breaking of a single C–H bond in CH_4. The present work provides much more complete full CI potential energy curves, with a much larger basis set (aug-cc-pVQZ) in the case of BH. The role of spin contamination in some unrestricted perturbation theory and coupled-cluster descriptions of bond breaking in these molecules has previously been studied by Chen and Schlegel[26] and by Krylov,[15] who compared to earlier, more approximate benchmark potential energy curves. The present results should prove useful in the calibration of new theoretical methods for bond breaking.

II. THEORETICAL APPROACH

The molecules considered in this study are BH, HF, and CH_4. For BH, we have used both standard and augmented correlation consistent polarized valence quadruple zeta basis sets, denoted by cc-pVQZ and aug-cc-pVQZ.[27,28] The augmented basis set adds an extra set of diffuse functions for each angular momentum in the basis. We have used the standard split-valence polarized double-zeta basis sets 6-31G* for methane and 6-31G** for HF.[29,30] The 6-31G** basis was recently shown to be among the best polarized double-zeta basis sets for full CI benchmarking.[31] We have performed MP2,[19] CCSD,[20] CCSD(T),[22] FCI, and B3LYP[23,24] calculations for all three molecules over a wide range of geometries. FCI and all computations using restricted orbitals (except for B3LYP) are obtained using the PSI 3.0 package,[32] and all other computations employed Q-CHEM 2.0.[33] Full CI procedures employed the DETCI module of PSI.[34] For convenience, methods using unrestricted orbitals are denoted with a prefix ''U,'' as in UMP2, UCCSD, etc. The frozen core approximation has been used for all three molecules. For BH, B3LYP results are not reported because of a limitation in the Q-CHEM program for density-functional theory computations with quadruple zeta basis sets. Results

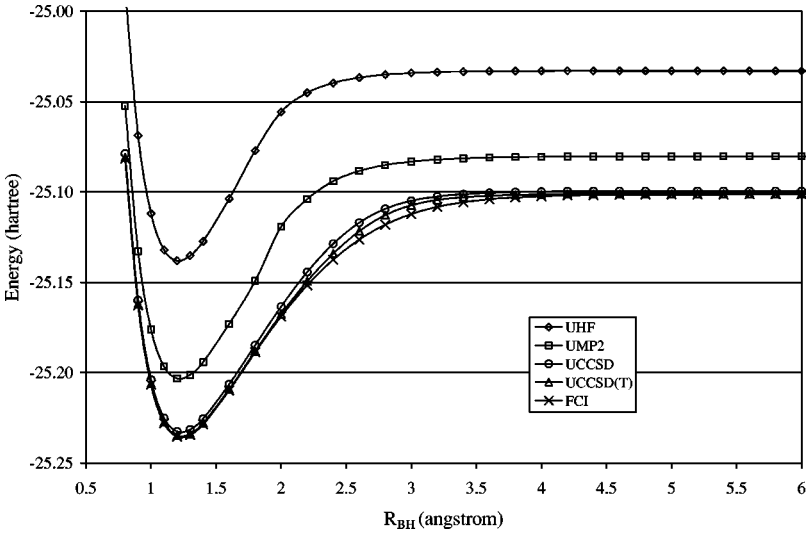

FIG. 2. Potential energy curves for BH in an aug-cc-pVQZ basis using various approximate correlation methods with a UHF reference.

TABLE I. Full CI total energies and errors for approximate correlation methods (hartrees) for BH using the aug-cc-pVQZ basis.

R(HF)/Å	FCI	RHF	MP2	CCSD	CCSD(T)
0.8	−25.081 635	0.103 300	0.024 536	0.002 575	0.000 486
0.9	−25.162 689	0.102 950	0.024 592	0.002 570	0.000 482
1.0	−25.206 668	0.103 003	0.024 792	0.002 592	0.000 483
1.1	−25.227 984	0.103 417	0.025 140	0.002 639	0.000 487
1.2	−25.235 431	0.104 163	0.025 642	0.002 710	0.000 496
1.3	−25.234 478	0.105 216	0.026 302	0.002 809	0.000 511
1.4	−25.228 572	0.106 550	0.027 122	0.002 935	0.000 532
1.6	−25.209 827	0.109 979	0.029 250	0.003 284	0.000 592
1.8	−25.188 685	0.114 305	0.032 035	0.003 782	0.000 676
2.0	−25.168 838	0.119 441	0.035 486	0.004 444	0.000 761
2.2	−25.151 628	0.125 375	0.039 626	0.005 288	0.000 803
2.4	−25.137 469	0.132 146	0.044 472	0.006 320	0.000 711
2.6	−25.126 368	0.139 762	0.049 980	0.007 516	0.000 332
2.8	−25.118 093	0.148 134	0.056 000	0.008 818	−0.000 539
3.0	−25.112 226	0.157 031	0.062 240	0.010 123	−0.002 119
3.2	−25.108 253	0.166 129	0.068 328	0.011 326	−0.004 532
3.4	−25.105 660	0.175 101	0.073 901	0.012 357	−0.007 735
3.6	−25.104 013	0.183 682	0.078 672	0.013 188	−0.011 519
3.8	−25.102 983	0.191 702	0.082 459	0.013 828	−0.015 576
4.0	−25.102 345	0.199 075	0.085 182	0.014 305	−0.019 594
4.2	−25.101 951	0.205 779	0.086 829	0.014 652	−0.023 320
4.4	−25.101 708	0.211 833	0.087 439	0.014 901	−0.026 595
4.6	−25.101 557	0.217 275	0.087 080	0.015 077	−0.029 346
4.8	−25.101 464	0.222 159	0.085 837	0.015 200	−0.031 566
5.0	−25.101 405	0.226 538	0.083 797	0.015 285	−0.033 294
5.2	−25.101 367	0.230 468	0.081 052	0.015 343	−0.034 589
5.4	−25.101 342	0.233 998	0.077 690	0.015 383	−0.035 520
5.6	−25.101 326	0.237 175	0.073 793	0.015 409	−0.036 160
5.8	−25.101 316	0.240 041	0.069 438	0.015 427	−0.036 569
6.0	−25.101 308	0.242 633	0.064 695	0.015 438	−0.036 800

TABLE II. Error vs FCI for BH (hartrees) using the aug-cc-pVQZ basis.

R(HF)/Å	UHF	UMP2	UCCSD	UCCSD(T)
0.8	0.093 718	0.029 366	0.002 847	0.000 701
0.9	0.093 966	0.029 847	0.002 833	0.000 685
1.0	0.094 722	0.030 523	0.002 844	0.000 669
1.1	0.095 894	0.031 347	0.002 878	0.000 652
1.2	0.097 414	0.032 288	0.002 936	0.000 637
1.3	0.099 233	0.033 321	0.003 020	0.000 623
1.4	0.101 307	0.034 426	0.003 132	0.000 611
1.6	0.106 086	0.036 810	0.003 452	0.000 600
1.8	0.111 529	0.039 420	0.003 921	0.000 609
2.0	0.113 119	0.049 633	0.005 414	0.001 196
2.2	0.106 530	0.047 664	0.007 325	0.002 196
2.4	0.097 833	0.043 484	0.008 814	0.003 401
2.6	0.089 716	0.038 020	0.009 385	0.004 671
2.8	0.083 080	0.033 000	0.008 780	0.005 301
3.0	0.078 119	0.029 043	0.007 354	0.004 881
3.2	0.074 650	0.026 208	0.005 769	0.003 847
3.4	0.072 341	0.024 303	0.004 450	0.002 778
3.6	0.070 854	0.023 078	0.003 501	0.001 937
3.8	0.069 917	0.022 311	0.002 872	0.001 354
4.0	0.069 333	0.021 839	0.002 473	0.000 977
4.2	0.069 047	0.021 695	0.002 425	0.000 948
4.4	0.068 790	0.021 467	0.002 201	0.000 728
4.6	0.068 633	0.021 329	0.002 067	0.000 595
4.8	0.068 535	0.021 246	0.001 986	0.000 516
5.0	0.068 474	0.021 195	0.001 937	0.000 468
5.2	0.068 435	0.021 163	0.001 907	0.000 438
5.4	0.068 410	0.021 144	0.001 889	0.000 420
5.6	0.068 394	0.021 132	0.001 877	0.000 410
5.8	0.068 383	0.021 125	0.001 870	0.000 403
6.0	0.068 376	0.021 120	0.001 866	0.000 399

have been obtained using the largest abelian subgroup, which is C_{2v} for BH and HF and C_s for CH_4. For methane, the potential energy curve was obtained by altering the length of a single C–H bond while keeping the remaining three C–H bonds at their equilibrium bond length (1.086 Å)[35] and the HCH angles at the tetrahedral value. The number of determinants in the full CI wave functions are 15,132,412 (aug-cc-pVQZ BH); 3,756,816 (6-31G** HF); and 26,755,625 (6-31G* CH_4).

III. RESULTS AND DISCUSSION

The potential energy curves for the ground state of BH using the aug-cc-pVQZ basis set are displayed in Figs. 1 and 2 for RHF and UHF references, respectively. Tables I and II provide full CI benchmark energies and the relative errors for the different correlation methods considered. These errors are presented graphically in Fig. 3. Results using the nonaugmented basis cc-pVQZ were very similar and are available

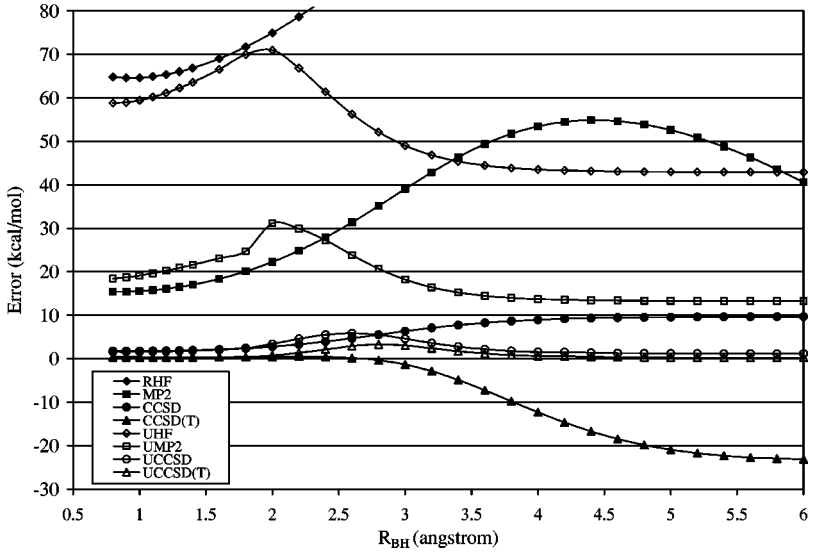

FIG. 3. Errors in potential energies for BH using various approximate correlation methods with an aug-cc-pVQZ basis.

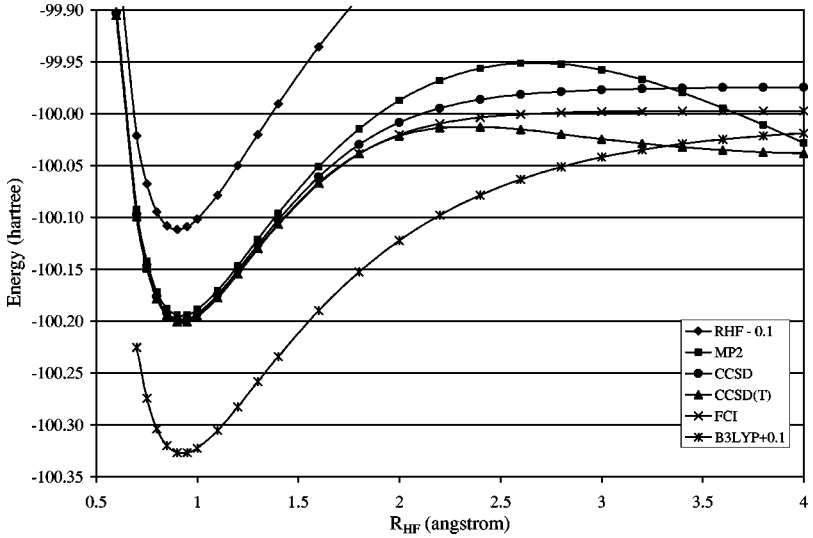

FIG. 4. Potential energy curves for HF in a 6-31G** basis using full configuration interaction and various approximate correlation methods with restricted orbitals.

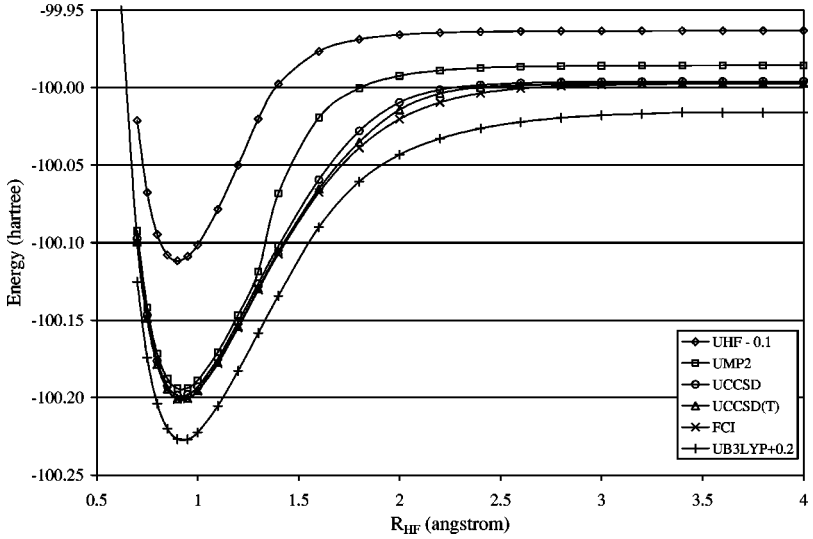

FIG. 5. Potential energy curves for HF in a 6-31G** basis using various approximate correlation methods with unrestricted orbitals.

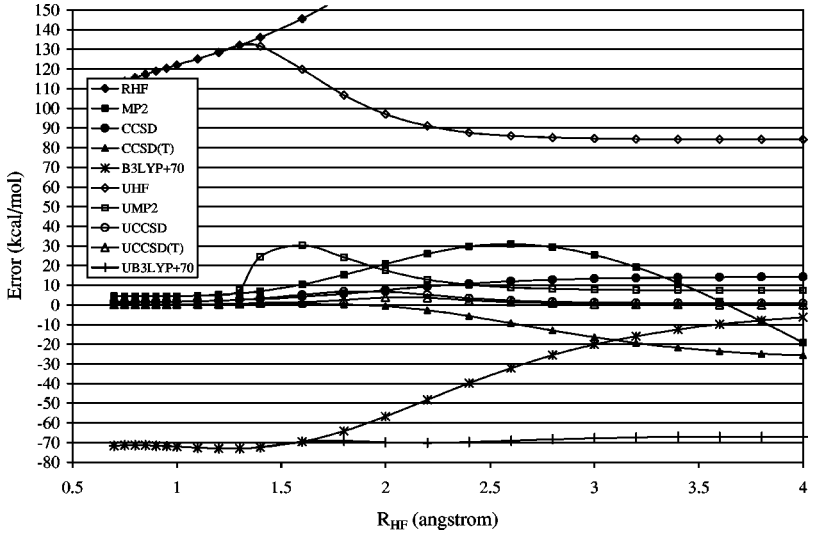

FIG. 6. Errors in potential energies for HF using various approximate correlation methods with a 6-31G** basis. B3LYP and UB3LYP error curves have been shifted up by 70 kcal mol^{-1}.

TABLE III. Full CI total energies and errors for approximate correlation methods (hartrees) for HF using the 6-31G** basis.

R(HF)/Å	FCI	RHF	MP2	CCSD	CCSD(T)	B3LYP
0.7	−100.099 608	0.178 509	0.007 192	0.002 177	0.000 284	−0.225 693
0.75	−100.148 949	0.181 376	0.007 112	0.002 254	0.000 316	−0.225 268
0.8	−100.178 698	0.184 127	0.007 040	0.002 339	0.000 351	−0.225 175
0.85	−100.194 685	0.186 782	0.006 984	0.002 435	0.000 388	−0.225 321
0.9	−100.201 051	0.189 360	0.006 957	0.002 541	0.000 426	−0.225 664
0.95	−100.200 742	0.191 886	0.006 973	0.002 659	0.000 466	−0.226 100
1.0	−100.195 856	0.194 385	0.007 046	0.002 794	0.000 507	−0.226 564
1.1	−100.177 901	0.199 407	0.007 416	0.003 120	0.000 592	−0.227 422
1.2	−100.154 778	0.204 653	0.008 169	0.003 536	0.000 680	−0.227 920
1.3	−100.130 510	0.210 354	0.009 395	0.004 061	0.000 770	−0.227 833
1.4	−100.107 251	0.216 722	0.011 173	0.004 719	0.000 853	−0.226 984
1.6	−100.067 574	0.232 020	0.016 561	0.006 524	0.000 901	−0.222 488
1.8	−100.038 851	0.250 967	0.024 250	0.009 022	0.000 452	−0.213 900
2.0	−100.020 326	0.272 872	0.033 203	0.011 957	−0.001 117	−0.202 035
2.2	−100.009 516	0.296 068	0.041 523	0.014 821	−0.004 311	−0.188 487
2.4	−100.003 626	0.318 633	0.047 267	0.017 210	−0.009 067	−0.175 015
2.6	−100.000 541	0.339 220	0.049 193	0.019 005	−0.014 790	−0.162 857
2.8	−99.998 957	0.357 234	0.046 877	0.020 276	−0.020 728	−0.152 310
3.0	−99.998 147	0.372 578	0.040 506	0.021 153	−0.026 270	−0.143 749
3.2	−99.997 728	0.385 410	0.030 621	0.021 753	−0.031 035	−0.136 993
3.4	−99.997 509	0.396 010	0.017 907	0.022 164	−0.034 845	−0.131 480
3.6	−99.997 395	0.404 702	0.003 045	0.022 444	−0.037 679	−0.127 348
3.8	−99.997 337	0.411 813	−0.013 353	0.022 634	−0.039 627	−0.124 166
4.0	−99.997 309	0.417 646	−0.030 787	0.022 761	−0.040 843	−0.121 620

from the authors. One striking feature of the results is the very poor behavior of MP2 and CCSD(T) at large distances when using an RHF reference. The MP2 energies diverge toward negative infinity, and the CCSD(T) energies drop below FCI around 3 Å and appear to level off around 6 Å at a value more than 20 kcal mol^{-1} below the FCI dissociation limit. These methods are able to produce energies below the FCI energy because they do not employ a symmetric expectation value formula for the energy, and hence they are not subject to the variational theorem. The poor performance of MP2 and CCSD(T) arises from the inapplicability of nondegenerate perturbation theory in cases of strong near-degeneracies as occur at large bond distances. RHF CCSD appears to be immune to these difficulties in this case, providing energies which never drop below FCI. However, the good performance of CCSD near equilibrium (absolute en-

TABLE IV. Error vs FCI for HF (hartrees) using the 6-31G** basis.

R(HF)/Å	UHF	UMP2	UCCSD	UCCSD(T)	UB3LYP
0.7	0.178 509	0.007 192	0.002 177	0.000 284	−0.225 693
0.75	0.181 376	0.007 112	0.002 254	0.000 316	−0.225 268
0.8	0.184 127	0.007 040	0.002 339	0.000 351	−0.225 175
0.85	0.186 782	0.006 984	0.002 435	0.000 388	−0.225 321
0.9	0.189 360	0.006 957	0.002 540	0.000 426	−0.225 664
0.95	0.191 886	0.006 973	0.002 659	0.000 466	−0.226 100
1.0	0.194 385	0.007 046	0.002 794	0.000 507	−0.226 564
1.1	0.199 407	0.007 416	0.003 119	0.000 592	−0.227 422
1.2	0.204 654	0.008 169	0.003 536	0.000 680	−0.227 920
1.3	0.210 323	0.011 937	0.004 082	0.000 817	−0.227 833
1.4	0.209 535	0.039 107	0.005 179	0.001 508	−0.226 984
1.6	0.190 964	0.048 227	0.008 184	0.002 334	−0.222 448
1.8	0.169 998	0.038 544	0.010 875	0.003 873	−0.221 766
2.0	0.154 528	0.027 967	0.010 800	0.006 085	−0.222 973
2.2	0.145 003	0.020 653	0.008 142	0.005 720	−0.223 331
2.4	0.139 706	0.016 391	0.005 362	0.003 819	−0.222 661
2.6	0.136 920	0.014 103	0.003 505	0.002 209	−0.221 625
2.8	0.135 496	0.012 925	0.002 455	0.001 223	−0.220 444
3.0	0.134 779	0.012 333	0.001 903	0.000 689	−0.219 649
3.2	0.134 423	0.012 042	0.001 625	0.000 416	−0.219 193
3.4	0.134 249	0.011 901	0.001 488	0.000 281	−0.218 401
3.6	0.134 166	0.011 834	0.001 424	0.000 217	−0.218 653
3.8	0.134 127	0.011 804	0.001 394	0.000 188	−0.218 661
4.0	0.134 110	0.011 791	0.001 381	0.000 175	−0.218 470

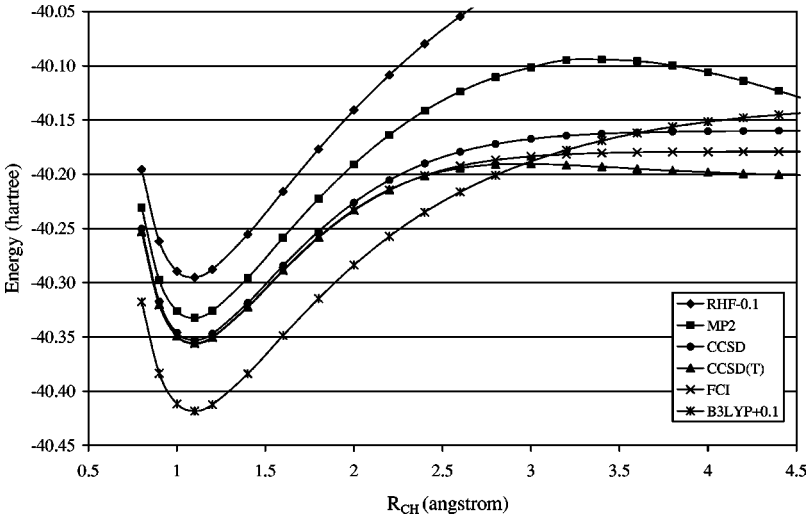

FIG. 7. Potential energy curves for CH_4 in a 6-31G* basis using full configuration interaction and various approximate correlation methods with restricted orbitals.

ergy errors of less than 2 kcal mol^{-1}) degrades significantly for larger bond distances and errors become more than 9 kcal mol^{-1} near dissociation.

Methods using a UHF reference perform significantly better in general, which is not surprising given that UHF is able to dissociate BH at least qualitatively correctly, unlike RHF. BH is unusual in that it is a closed-shell molecule with a UHF solution below the RHF solution even at the equilibrium geometry. UHF and UMP2 both significantly underestimate the dissociation energy, by ~18 and 7 kcal mol^{-1}, respectively. The UMP2 potential energy curve has an unusual shape in the intermediate bond breaking region, with the energy rising too rapidly around 2 Å and eventually leveling off to a dissociation limit which is too low. It is interesting to note that the error for UMP2 is larger than for restricted MP2 around equilibrium, and this difference increases in the intermediate bond breaking region to around 9 kcal mol^{-1}. Near 2.4 Å the MP2 and UMP2 error curves intersect, and the UMP2 errors become smaller at larger internuclear distances.

The unrestricted CCSD and CCSD(T) results are much better and match full CI very closely around equilibrium and near dissociation. Like UMP2, they also rise too rapidly in the intermediate region, although not as severely. There is a small region of intermediate geometries (2.2–2.6 Å) in which errors for CCSD with unrestricted orbitals becomes noticeably larger than CCSD with restricted orbitals, although the difference is much less (around 1 kcal mol^{-1}) than for MP2 versus UMP2.

To help quantify how well the approximate methods parallel the full CI potential energy curves, we have computed ''nonparallelity'' errors (NPE) for each approximate method. This error is defined as the difference between the absolute maximum and minimum deviations from the FCI potential curve over the points considered. The NPE would, therefore, be zero if a curve differed from the FCI curve by a constant shift. The NPE's are tabulated in Table VII, along with the minimum and maximum errors. Generally, the smallest errors occur near equilibrium for RHF references, but at the dissociation limit for UHF references. NPE's are not given for RHF and restricted MP2 and B3LYP, since the maximum error is not well defined for these cases. For BH, we find that unrestricted orbitals give much smaller NPE's than restricted orbitals, but the errors remain fairly large, around 5 and 3

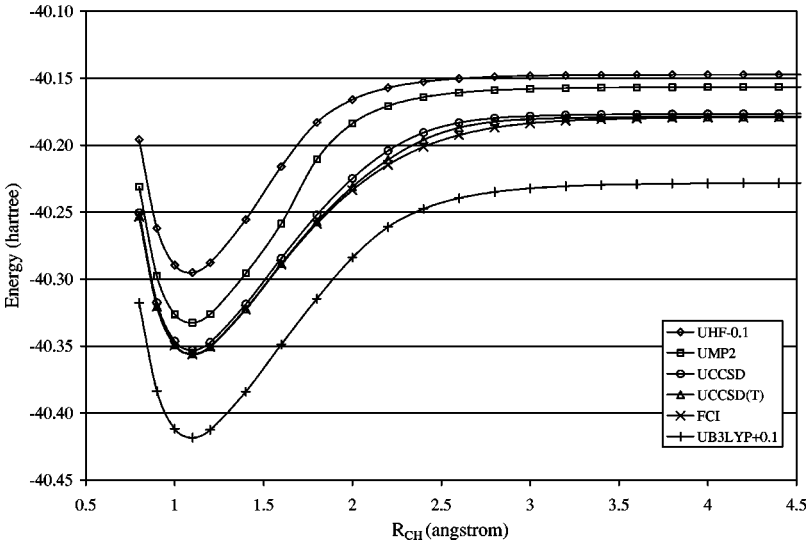

FIG. 8. Potential energy curves for CH_4 in a 6-31G* basis using various approximate correlation methods with unrestricted orbitals.

TABLE V. Full CI total energies and errors for approximate correlation methods (hartrees) for CH_4 using the 6-31G* basis.

R(HF)/Å	FCI	RHF	MP2	CCSD	CCSD(T)	B3LYP
0.8	−40.253 342	0.157 564	0.022 491	0.002 934	0.000 406	−0.164 354
0.9	−40.320 513	0.158 587	0.022 772	0.003 024	0.000 416	−0.163 074
1.0	−40.349 369	0.159 802	0.023 179	0.003 139	0.000 430	−0.162 354
1.1	−40.356 202	0.161 219	0.023 745	0.003 285	0.000 449	−0.162 013
1.2	−40.350 579	0.162 871	0.024 515	0.003 470	0.000 472	−0.161 852
1.4	−40.322 605	0.167 125	0.026 867	0.003 983	0.000 537	−0.161 383
1.6	−40.289 114	0.173 161	0.030 580	0.004 748	0.000 622	−0.159 666
1.8	−40.258 549	0.181 541	0.035 834	0.005 841	0.000 697	−0.156 035
2.0	−40.233 555	0.192 524	0.042 646	0.007 312	0.000 674	−0.150 357
2.2	−40.214 618	0.205 980	0.050 799	0.009 116	0.000 373	−0.142 795
2.4	−40.201 257	0.221 377	0.059 725	0.011 105	−0.000 444	−0.133 774
2.6	−40.192 439	0.237 891	0.068 541	0.013 048	−0.001 967	−0.123 953
2.8	−40.186 932	0.254 630	0.076 276	0.014 749	−0.004 200	−0.114 069
3.0	−40.183 629	0.270 847	0.082 108	0.016 109	−0.006 936	−0.104 641
3.2	−40.181 699	0.306 109	0.086 993	0.017 125	−0.009 856	−0.096 071
3.4	−40.180 583	0.299 797	0.086 181	0.017 849	−0.012 659	−0.088 552
3.6	−40.179 941	0.312 018	0.084 199	0.018 351	−0.015 147	−0.082 097
3.8	−40.179 569	0.322 621	0.079 783	0.018 695	−0.017 231	−0.076 739
4.0	−40.179 356	0.331 653	0.073 306	0.018 929	−0.018 911	−0.072 366
4.2	−40.179 234	0.339 239	0.065 196	0.019 091	−0.020 229	−0.068 856
4.4	−40.179 167	0.345 551	0.055 866	0.019 205	−0.021 245	−0.066 080
4.6	−40.179 132	0.350 782	0.045 677	0.019 285	−0.022 020	−0.063 917

kcal mol^{-1} for CCSD and CCSD(T), respectively. Although CCSD was superior to CCSD(T) when restricted orbitals were used, with unrestricted orbitals, CCSD(T) is once again more reliable than CCSD.

Potential energy curves for HF in a 6-31G** basis are given in Figs. 4 and 5 for restricted and unrestricted orbitals, respectively. Errors against full CI are presented in Fig. 6 and in Tables III and IV. The potential energy curves follow the same trends as in BH, except that the UHF solution now matches RHF up to a certain critical bond length (around 1.4 Å), which is the more typical situation. Again, restricted MP2 diverges to negative infinity for large bond distances, and restricted CCSD(T) gives energies which are far too low at dissociation. Unrestricted orbitals generally improve the MP2 and coupled-cluster results except for the intermediate region around the RHF–UHF instability point, where they introduce a slightly larger error for UCCSD and a significantly larger error for UMP2. The nonparallelity errors in Table VII show similar trends as for BH, but they are uniformly larger (NPE's for restricted CCSD, UHF, and UMP2 are all larger by several kcal mol^{-1}). For HF, we have also obtained results using the popular B3LYP density-functional

TABLE VI. Error vs FCI for CH_4 (hartrees) using the 6-31G* basis.

R(HF)/Å	UHF	UMP2	UCCSD	UCCSD(T)	UB3LYP
0.8	0.157 564	0.022 491	0.002 934	0.000 406	−0.164 350
0.9	0.158 587	0.022 772	0.003 024	0.000 416	−0.163 063
1.0	0.159 802	0.023 179	0.003 139	0.000 430	−0.162 373
1.1	0.161 219	0.023 745	0.003 285	0.000 450	−0.162 049
1.2	0.162 871	0.024 515	0.003 470	0.000 472	−0.161 902
1.4	0.167 125	0.026 867	0.003 983	0.000 537	−0.161 411
1.6	0.173 161	0.030 580	0.004 748	0.000 622	−0.159 665
1.8	0.175 531	0.048 044	0.006 499	0.001 430	−0.156 036
2.0	0.167 593	0.049 781	0.008 735	0.002 415	−0.150 375
2.2	0.157 438	0.043 895	0.010 460	0.003 727	−0.146 484
2.4	0.148 668	0.037 132	0.010 663	0.005 222	−0.146 239
2.6	0.142 271	0.031 736	0.009 220	0.005 502	−0.147 120
2.8	0.138 053	0.028 042	0.007 176	0.004 451	−0.148 004
3.0	0.135 442	0.025 717	0.005 437	0.003 107	−0.148 587
3.2	0.133 889	0.024 325	0.004 240	0.002 048	−0.148 898
3.4	0.132 990	0.023 520	0.003 497	0.001 352	−0.149 041
3.6	0.132 479	0.023 064	0.003 060	0.000 932	−0.149 082
3.8	0.132 194	0.022 811	0.002 813	0.000 691	−0.149 086
4.0	0.132 038	0.022 674	0.002 678	0.000 558	−0.149 081
4.2	0.131 956	0.022 602	0.002 606	0.000 487	−0.148 954
4.4	0.131 913	0.022 565	0.002 569	0.000 450	−0.149 057
4.6	0.131 892	0.022 547	0.002 550	0.000 432	−0.149 056

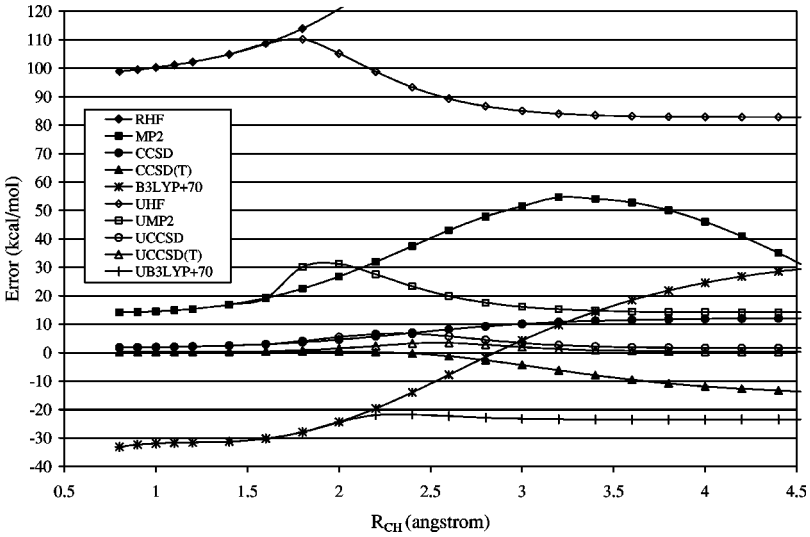

FIG. 9. Errors in potential energies for CH_4 using various approximate correlation methods with a 6-31G* basis. B3LYP and UB3LYP error curves have been shifted up by 70 kcal mol^{-1}.

method. The B3LYP energies are much lower than full CI and the B3LYP curves have been shifted upward in Figs. 4 and 5 for easier comparison to the wave function based methods. Although B3LYP exhibits large errors for restricted orbitals, unrestricted B3LYP remains fairly parallel to the full CI curve. The NPE of UB3LYP and UCCSD are both about 6 kcal mol^{-1}; of the methods considered, only UCCSD(T) provides a better result (3.7 kcal mol^{-1}).

Potential energy curves for CH_4 in a 6-31G* basis are presented in Figs. 7 and 8; errors are given in Tables V and VI and displayed in Fig. 9. Although the errors for restricted CCSD and CCSD(T) are a mere 3.3 and 0.4 millihartree around equilibrium, they increase to around 19 and −22 millihartree, respectively, around the dissociation limit (4.6 Å). The trends in the curves are very similar as for HF, although the difference between MP2 and UMP2 near the RHF–UHF instability is smaller than in HF and is more similar to that in BH. The quality of UB3LYP is not as good for CH_4 as for HF, with the NPE growing to more than 11 kcal mol^{-1}. UCCSD and UCCSD(T) are the two best methods in this case, with NPE's of about 5 and 3 kcal mol^{-1}, respectively.

The observation that unrestricted orbitals lead to larger errors for MP2 and CCSD in the intermediate bond breaking region deserves further discussion. It should be pointed out once again that in this study we are examining the breaking of bonds to hydrogen atoms, which ought to be the simplest case for single-reference methods. Indeed, Krylov[15] has shown that in the unusually challenging case of F_2, unrestricted orbitals can cause CCSD to exhibit unphysical behavior with very large errors in the bond breaking region. Ideally, one would like some way to obtain results like CCSD with restricted orbitals around equilibrium and in the intermediate region, with a smooth transition to UCCSD at the dissociation limit. Fortunately, there is a way to achieve this. Purvis *et al.*[36] suggested that orbitals which minimized the CCD energy might prove useful in going between limits like this for bond breaking problems. This optimized-orbital coupled-cluster doubles (OO-CCD) approach was first tested by Purvis and Bartlett[20] and examined more fully by Scuseria and Schaefer,[37] with the first efficient implementation and examination of molecular properties by Sherrill *et al.*[38] Consistent with previous work,[15] we find that OO-CCD allowing

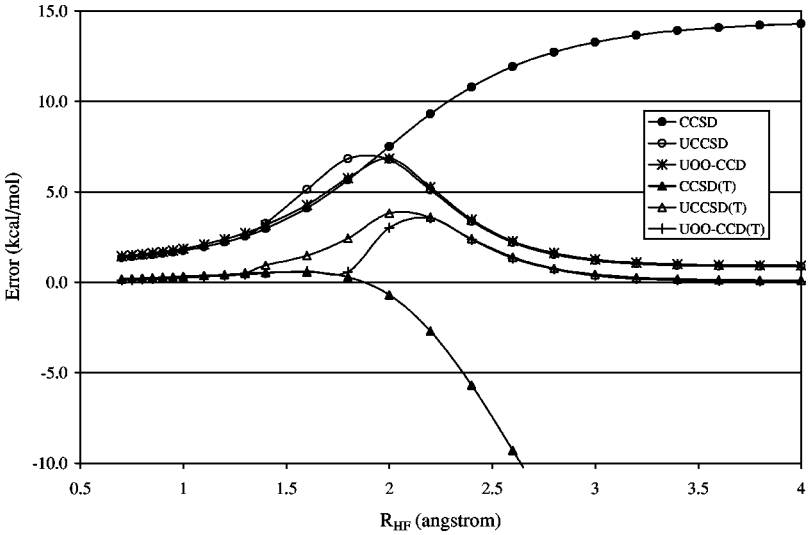

FIG. 10. Errors in potential energies for HF using the 6-31G** basis and coupled-cluster methods with restricted, unrestricted, and optimized orbitals.

TABLE VII. Maximum, minimum, and nonparallelity errors (NPE), in kcal mol^{-1}, for the BH, HF and CH_4 molecules. Values in the parentheses indicate the corresponding internuclear distances.[a]

	BH					HF					CH_4				
Method	Max		Min		NPE	Max		Min		NPE	Max		Min		NPE
RHF	⋯		64.6	(0.9)	⋯	⋯		112.0	(0.7[b])	⋯	⋯	98.9	(0.8[b])		⋯
MP2	⋯		15.4	(0.8[b])	⋯	⋯		4.4	(0.9)	⋯	⋯		14.1	(0.8[b])	⋯
CCSD	9.7	(6.0[b])	1.6	(0.9)	8.1	14.4	(5.0[b])	1.4	(0.7[b])	13.0	12.1	(4.6[b])	1.8	(0.8[b])	10.3
CCSD(T)	−23.1	(6.0[b])	0.2	(2.6)	23.3	−26.6	(4.8)	0.2	(0.7[b])	26.8	⋯		0.2	(2.2)	⋯
B3LYP	n/a					⋯		−72.5	(5.0[b])	⋯	⋯		−40.1	(4.6[b])	⋯
UHF	71.0	(2.0)	42.9	(6.0[b])	28.1	132.0	(1.3)	84.1	(5.0[b])	47.8	110.1	(1.8)	82.8	(4.6[b])	27.4
UMP2	31.1	(2.0)	13.3	(6.0[b])	17.9	30.3	(1.6)	4.4	(0.9)	25.9	31.2	(2.0)	14.1	(0.8[b])	17.1
UCCSD	5.9	(2.6)	1.2	(6.0[b])	4.7	6.8	(1.8)	0.9	(5.0[b])	6.0	6.7	(2.4)	1.6	(4.6[b])	5.1
UCCSD(T)	3.3	(2.8)	0.3	(6.0[b])	3.1	3.8	(2.0)	0.1	(5.0[b])	3.7	3.5	(2.6)	0.3	(0.8[b])	3.2
UB3LYP	n/a					−143.0	(1.2)	−137.1	(5.0[b])	5.9	−103.1	(0.8)	−91.8	(2.4)	11.4

[a]Errors with the largest maximum and minimum absolute value are given. Some values for methods with very large or divergent errors are not listed. The NPE is the difference between the magnitudes of the maximum and minimum errors.
[b]Error for largest or smallest bond length considered.

unrestricted orbitals (denoted here UOO-CCD) connects smoothly between the CCSD and UCCSD behaviors at short and long distances, respectively. Figure 10 demonstrates results for UOO-CCD and UOO-CCD(T) for the HF molecule. Although UOO-CCD does not include single excitations, the orbital optimization plays essentially the same role; UOO–CCD acts remarkably similar to CCSD to the left of the bond breaking region, and it switches smoothly to near UCCSD behavior at long distances. Although the error for UOO–CCD is usually smaller in the intermediate region, the maximum error is unfortunately about the same as in UCCSD. We also tested OO-CCD with restricted orbitals but found that it does not improve significantly upon CCSD with RHF orbitals. UOO-CCD(T) behaves in the same qualitative manner as UOO-CCD, acting as CCSD(T) before the bond breaking region, and as UCCSD(T) afterward. UOO-CCD(T) shifts from restricted to unrestricted behavior over the range $R_{HF} = 1.8–2.2$ Å, compared to 1.4–2.0 Å for OO-CCD. Although the errors for UOO-CCD(T) are generally less than for UCCSD(T), the maximum errors, near 2.0 Å, are nearly the same (3.5 and 3.8 kcal mol^{-1}, respectively).

IV. CONCLUSIONS

In this paper we have analyzed the performance of the MP2, CCSD, CCSD(T), and B3LYP methods for bond breaking reactions in the BH, HF, and CH_4 molecules by comparison to full CI results. In all three cases, in addition to the anticipated divergence of RHF and restricted MP2, we see very large errors in UHF and UMP2 at intermediate distances, and in restricted CCSD(T) at large distances. CCSD and especially MP2 exhibit larger errors with unrestricted than restricted Hartree–Fock orbitals in the intermediate bond breaking region. UB3LYP appears to improve upon UMP2 but is inferior to UCCSD and UCCSD(T) for breaking bonds to hydrogen. Among the investigated models, unrestricted CCSD and CCSD(T) are preferred because they remain the most parallel to the full CI curve for all three molecules. However, it must be noted that all of the methods considered give rather large nonparallelity errors, about 3 to 4 kcal mol^{-1} for UCCSD(T), and larger for the other methods. Accounting for orbital relaxation by variational optimization of the orbitals at the CCD level, rather than by single excitations, gives a method which behaves as well as CCSD at short internuclear distances and as well as UCCSD at large distances. The resulting UOO-CCD and UOO-CCD(T) approaches clearly improve upon their counterparts based on Hartree–Fock orbitals, but have nearly the same maximum errors as UCCSD and UCCSD(T), respectively. Breaking bonds to atoms other than hydrogen is expected to be even more challenging for single-reference methods, and we will pursue such systems in future work.

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[1] K. Andersson and B. O. Roos, Multiconfigurational second-order perturbation theory, in *Modern Electronic Structure Theory*, edited by D. R. Yarkony, of *Advanced Series in Physical Chemistry* (World Scientific, Singapore, 1995), Vol. 2, pp. 55–109.
[2] C. W. Bauschlicher, S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, J. Chem. Phys. **85**, 1469 (1986).
[3] C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys. **86**, 5600 (1987).
[4] C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys. **86**, 1420 (1987).
[5] C. W. Bauschlicher and S. R. Langhoff, Chem. Phys. Lett. **135**, 67 (1987).
[6] C. W. Bauschlicher and P. R. Taylor, J. Chem. Phys. **85**, 2779 (1986).
[7] T. van Mourik and J. H. van Lenthe, J. Chem. Phys. **102**, 7479 (1995).
[8] J. Olsen, P. Jørgensen, H. Koch, A. Balková, and R. J. Bartlett, J. Chem. Phys. **104**, 8007 (1996).
[9] A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 10669 (1998).
[10] H. Larsen, J. Olsen, P. Jørgensen, and O. Christiansen, J. Chem. Phys. **113**, 6677 (2000).
[11] H. Larsen, J. Olsen, P. Jørgensen, and O. Christiansen, J. Chem. Phys. **114**, 10985 (2001).
[12] A. I. Krylov, C. D. Sherrill, and M. Head-Gordon, J. Chem. Phys. **113**, 6509 (2000).
[13] W. D. Laidig and R. J. Bartlett, Chem. Phys. Lett. **104**, 424 (1984).
[14] S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **113**, 3548 (2000).
[15] A. I. Krylov, J. Chem. Phys. **113**, 6052 (2000).
[16] K. Kowalski and P. Piecuch, J. Chem. Phys. **113**, 18 (2000).

[17] K. Kowalski and P. Piecuch, Chem. Phys. Lett. **344**, 165 (2001).
[18] A. I. Krylov and C. D. Sherrill, J. Chem. Phys. **116**, 3194 (2002).
[19] J. A. Pople, S. Binkley, and R. Seeger, Int. J. Quantum Chem., Symp. **10**, 1 (1976).
[20] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[21] M. Rittby and R. J. Bartlett, J. Phys. Chem. **92**, 3033 (1988).
[22] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[23] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[24] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, J. Phys. Chem. **98**, 11623 (1994).
[25] F. B. Brown and D. G. Truhlar, Chem. Phys. Lett. **113**, 441 (1985).
[26] W. Chen and W. B. Schlegel, J. Chem. Phys. **101**, 5957 (1994).
[27] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[28] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[29] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).
[30] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).
[31] M. L. Abrams and C. D. Sherrill, J. Chem. Phys. (to be published).
[32] T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, PSI 3.0, development version, PSITECH, Inc., Watkinsville, GA, 1999.
[33] J. Kong, C. A. White, A. I. Krylov, *et al.*, J. Comput. Chem. **21**, 1532 (2000).
[34] C. D. Sherrill and H. F. Schaefer, The configuration interaction method: Advances in highly correlated approaches, in *Advances in Quantum Chemistry*, edited by P.-O. Löwdin (Academic, New York, 1999), Vol. 34, pp. 143–269.
[35] D. L. Gray and A. G. Robiette, Mol. Phys. **37**, 1901 (1979).
[36] G. D. Purvis, R. Shepard, F. B. Brown, and R. J. Bartlett, Int. J. Quantum Chem. **23**, 835 (1983).
[37] G. E. Scuseria and H. F. Schaefer, Chem. Phys. Lett. **142**, 354 (1987).
[38] C. D. Sherrill, A. I. Krylov, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 4171 (1998).